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RAMAN SPECTROSCOPY OF PASSIVE FILMS FORMED ON METAL SURFACES IN--ETC(U)

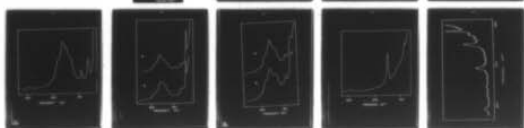
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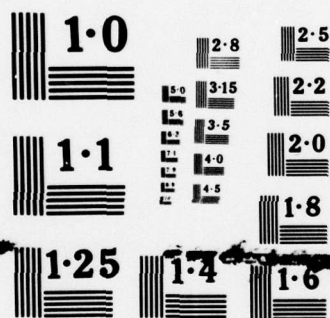
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RAMAN SPECTROSCOPY OF PASSIVE FILMS FORMED  
ON METAL SURFACES IN CORROSIVE ENVIRONMENTS

CONTRACT NUMBER: N00014-76-C-0889

ANNUAL REPORT

JANUARY 1977

SUBMITTED TO

OFFICE OF NAVAL RESEARCH

SUBMITTED BY

UNIVERSITY OF RHODE ISLAND  
KINGSTON, RHODE ISLAND 02881

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Richard W. /Thibeau, Arnon /Goldfarb

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ABSTRACT

In situ Raman spectra were obtained of passive films formed on metallic lead surfaces under freely corroding conditions in dilute hydrochloric acid and sodium hydroxide solutions. The spectra identified the coating formed in HCl solution as  $\text{PbCl}_2$  and that formed in NaOH solution as  $\text{PbO}$ . Passive film composition was the same in solutions containing dissolved oxygen as in deoxygenated solutions but the rate of film growth was much greater in the presence of oxygen. Spectra of the films immersed in solution were virtually identical to those of the same films in air.

The experimental program for passive films on lead was successfully completed. Investigations on passive films on iron surfaces were initiated.



#### PERSONNEL

This report covers research efforts by Dr. R. Heidersbach, Department of Ocean Engineering and Dr. Chris W. Brown and Mr. Richard W. Thibau of the Department of Chemistry, University of Rhode Island. Mr. Arnon Goldfarb, Department of Ocean Engineering was also employed on this project.

## INTRODUCTION

Raman spectroscopy provides very specific information on the identity and bonding of molecules, but it has been applied to surface studies only recently. Raman spectra have been used in catalysis investigations to characterize bonding between solid catalysts and absorbed species<sup>1,2</sup> by analyzing spectra of the molecules absorbed on high surface area powders<sup>3-5</sup>. Spectra have been obtained of compounds absorbed on electrode surfaces<sup>6,7</sup> and of fairly thin films of organic molecules sprayed on silver mirrors<sup>8,9</sup>; however, investigations of corrosion products formed on a metal surface have not been reported.

Raman spectroscopy is well suited to the study of corrosion products because spectra can be recorded while the specimen is corroding in an aqueous medium. Many other methods usually applied to the study of corrosion films such as electron diffraction, Auger spectroscopy, etc., require removal of the sample from solution before any information can be obtained, and this can cause possible structural or chemical changes in the surface layer. To be certain that no changes occur, the spectrum must be obtained in situ. Since water is a weak Raman scatterer it gives very little interference and spectra can be obtained as easily with the sample in water as with the water removed.

The purpose of the work reported here was to show that Raman scattering by passive films can be useful for the analysis of surface films of these compounds and that spectra of the samples immersed in aqueous solution are similar in quality and intensity to those obtained with the samples in air. Lead foil was allowed to corrode in controlled aqueous environments and Raman spectra of the surface were recorded.

## EXPERIMENTAL

Spectra were recorded with a Spex Industries Model 1401 double monochromator using a photon counting detection system. A Coherent Radiation Model 52G argon ion gas laser was used as the excitation source. Both the 488.0 nm and 514.5 nm wavelength laser lines were used and the power at the sample was less than 300 mW.

The optical schematic of a modern Raman spectrometer such as that used in this investigation is shown in Figure 1. The spectrometer consists of a laser, a sample compartment, an optical monochromator, and a detection system. The laser is located beneath the monochromator and the laser beam is directed by a mirror or series of mirrors to a sample. The scattered light is collected by a lens placed 90° to the sample and is focussed onto the entrance slits of the monochromator (side view). In our instrument we have a double optical monochromator (see top view). The light entering the slits (S) is collimated by a mirror (M) onto the grating (G) which disperses the light. Depending upon the angle of the grating with respect to the incident beam, a certain segment (band pass of light) is focussed onto the intermediate slits (S) by a collimating and a plane mirror. From the intermediate slits, the light goes through a second monochromator; plane mirror, collimating mirror, grating, collimating mirror, and exit slits. Finally the light reaches the detector, a photo-multiplier tube (PM). Each photon reach-

ing the PM tube is converted to an electrical signal which is amplified and then counted. The number of counts (number of photons) per selected time interval are converted to an analog signal which drives a pen on a strip chart recorder.

Spectra were recorded with lead foil samples clamped in place, immersed in a solution inside a Pyrex beaker, at angles of  $40-70^\circ$  from the vertical laser beam. Laser radiation entered through the bottom of the beaker and reflected off of the sample surface. Scattered light passed through the side of the beaker and was focussed at the entrance slit of the monochromator. For spectra of sample surfaces in air the same arrangement was used with the beaker of solution removed. Reference spectra of PbO and PbCl<sub>2</sub> powders were obtained with the powder in a Pyrex capillary tube.

The lead foil used was 1 mm in thickness and was supplied by Alfa Products, Inc., Danvers, Massachusetts at 99.9995% purity. It was cut into strips approximately 1 cm wide and cleaned of its oxide coating by immersing in warm, concentrated ammonium acetate solution and rinsing in distilled water prior to being placed in a corrosive solution. The solutions were made from reagent grade chemicals; 0.1 M HCl solution produced a PbCl<sub>2</sub> coating and 0.01 M NaOH solution produced the PbO coating. Each exposure was conducted in two ways; air saturated (sample immersed in solution with air bubbled through), and deoxygenated (nitrogen bubbled through the solution).

Successful completion of the experimental program for passive films formed on lead was followed by initial efforts to obtain Raman spectra for iron-based corrosion products.

Due to strong absorption at both 488.0 and 514.5 nm excitation wavelengths a good spectrum of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> could not be obtained with a capillary tube sample. A pure  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> pellet was formed by compressing the powdered compound (greater than 99% purity) at room temperature. In the sample compartment the pellet was held at an angle of approximately  $30^\circ$  from the laser beam so that, as with the lead foil samples, the greatest intensity of laser light was reflected away from the focussing lens by the smooth pellet surface. Only a part of the light scattered out of the main beam of light was directed into the monochromator.

## RESULTS AND DISCUSSION

Since a pure metal has no Raman spectrum the choice of lead for this study was made solely on the basis of the compounds it would form from aqueous corrosion. Lead compounds were expected to have good Raman scattering characteristics and argon ion laser frequencies are available which are not strongly absorbed by PbCl<sub>2</sub> and PbO.

### Reference Spectra

Figure 2 shows spectra of PbCl<sub>2</sub> and PbO powders recorded for reference and comparison. The very low frequency lattice vibrational bands were easily detected. Raman spectra of bands down to  $20\text{ cm}^{-1}$  can be recorded with no difficulty, however, to obtain infrared absorption spectra at similar frequencies special equipment is required.



From the spectrum of  $\text{PbCl}_2$  powder containing 0.95%  $\text{PbO}$  shown in Figure 3, it is clear that 1% or greater proportion of  $\text{PbO}$  in  $\text{PbCl}_2$  should be clearly visible. The strong  $\text{PbO}$  bands at 143 and 290  $\text{cm}^{-1}$  which do not coincide with  $\text{PbCl}_2$  bands are easily seen. This spectrum was recorded to show that we would be able to detect small amounts of oxide which might be formed when the metal is oxidized in a chloride solution. The opposite mixture, a small amount of  $\text{PbCl}_2$  mixed with a large amount of  $\text{PbO}$ , showed the Raman spectrum of  $\text{PbO}$  to be considerably stronger than that of  $\text{PbCl}_2$ . No bands due to the chloride could be seen in mixtures containing up to 16%  $\text{PbCl}_2$ . These spectra were recorded as preliminaries for possible studies of chloride enhanced corrosion to see if small amounts of the chloride would be detectable in an oxide layer. It is probable that the  $\text{PbO}$  dominates the spectra of mixtures because its electronic absorption band is much closer to the excitation frequencies used than that of  $\text{PbCl}_2$  and pre-resonance Raman enhancement of the  $\text{PbO}$  spectrum results.

#### $\text{PbCl}_2$ Spectra

Lead samples immersed in  $\text{HCl}$  solution slowly become covered by a dark gray coating which, when thick, appears crystalline. Spectra of surfaces with such a coating are shown in Figures 4 and 5. The spectra are virtually identical to that of pure  $\text{PbCl}_2$  powder. In acid solution lead metal should be oxidized to  $\text{Pb}^{++}$  which would enter the solution. The solubility of  $\text{PbCl}_2$  is low, however, so only a small amount of  $\text{Pb}^{++}$  ions may go into solution. Most of the oxidized lead forms the observed layer of  $\text{PbCl}_2$ . By comparison with the powder spectra it may be seen that if any  $\text{PbO}$  was formed it was less than 1% of the amount of  $\text{PbCl}_2$ .

As shown in Figure 4, the spectrum of lead immersed in deoxygenated  $\text{HCl}$  solution is very similar to that of lead exposed to an air saturated solution, the only difference is in the quality of the spectra. The aerated solution promotes faster oxidation of the sample, i.e., the chloride coating becomes thick enough to give a good Raman spectrum much faster in the aerated solution. The difference between the spectra in Figure 4 can be explained by a thicker  $\text{PbCl}_2$  layer on the aerated sample, i.e., a thicker layer giving more intense Raman bands.

Figure 5 shows the spectrum of a sample immersed in an aerated  $\text{HCl}$  solution for three days; this is clearly the spectrum of  $\text{PbCl}_2$ . The sample was then removed from the solution and allowed to dry in air. The spectrum of the dry sample is nearly identical to that of the sample in solution. There is no noticeable reduction of the quality or intensity of the Raman spectrum when it is recorded with the sample covered by an aqueous solution.

#### $\text{PbO}$ Spectra

In agreement with the Pourbaix diagram<sup>8</sup>, lead immersed in a basic solution (sodium hydroxide) is oxidized to  $\text{PbO}$ . This is confirmed by the spectrum in Figure 6. The gray coating formed on a lead surface gives a spectrum of  $\text{PbO}$ . Samples were exposed to aerated and deoxygenated solutions and the results, like those of the chloride exposures, were the same except for the rate of formation of the corrosion product layer. In aerated  $\text{NaOH}$  solution the oxide coating became thick enough to give a good Raman spectrum much more rapidly than in a deoxygenated solution of the same concentration.

Spectra of PbO were obtained using the 514.5 nm exciting wavelength. Use of the 488.0 nm line caused some decomposition and a poorer spectrum because the incident radiation was too strongly absorbed. Absorption of the exciting radiation was not a problem with PbCl<sub>2</sub> and the 488.0 nm line gave excellent results.

#### $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> Spectrum

It is not likely that  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (hematite) will be found in aqueous passive films. It is generally acknowledged<sup>3</sup> that  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (maghematite) is the form present<sup>9-11</sup>. Since corrosion product films are not well characterized and there are very few Raman spectra reported for oxides and hydroxides of iron, reference spectra of all iron compounds which might occur as a result of corrosion were desired. That of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, the first oxide examined, is shown in Figure 7. All seven bands reported in the single crystal Raman spectrum of Fe<sub>2</sub>O<sub>3</sub><sup>12</sup> can be seen.

#### CONCLUSION

Raman spectra can be obtained from surface films of corrosion products on a metal surface. There is very little difference in the intensity of spectra of coatings whether they are recorded with the metal in aqueous solution or in air, so Raman spectroscopy can be used to study aqueous corrosion products in situ.

Lead was chosen for these studies because of the Raman scattering characteristics of its compounds, but our intent is to apply this method to metals of greater importance such as iron and its alloys, and to study passive films and breakdown of passivation in aqueous media.

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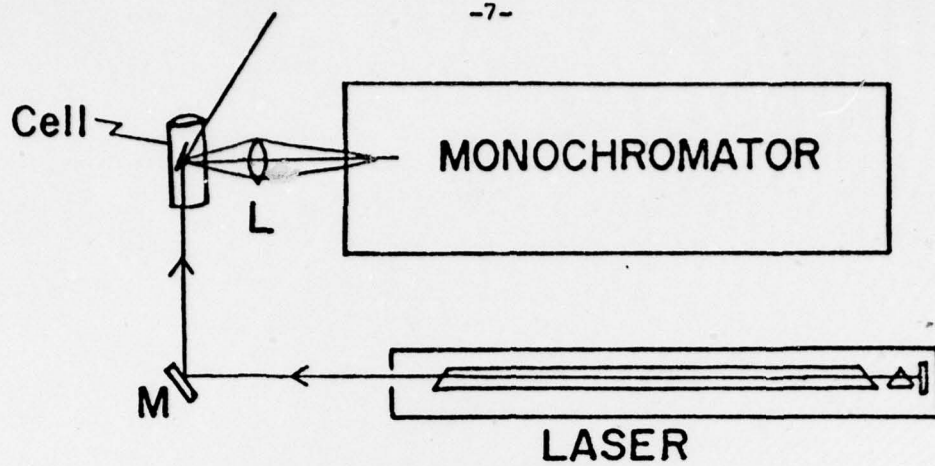
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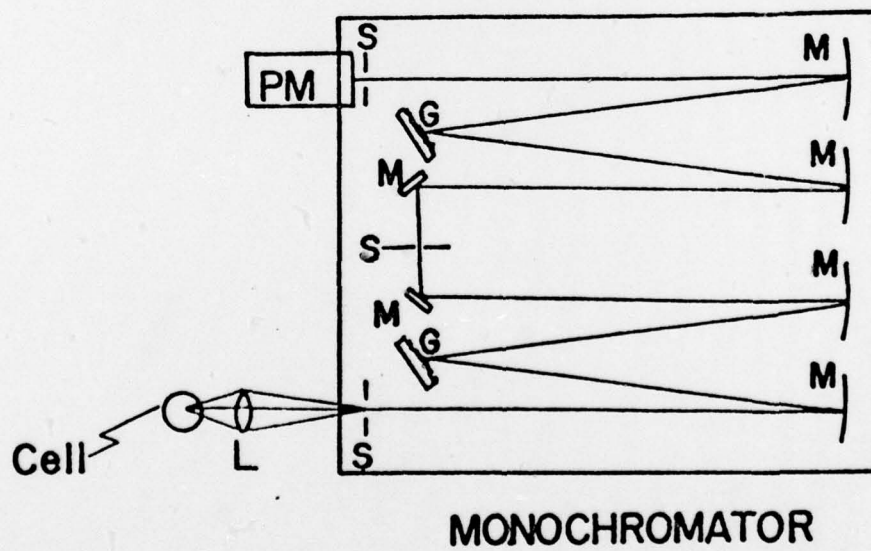
FIGURE CAPTIONS

- Figure 1. Optical schematic of Raman spectrometer.
- Figure 2. Raman spectra of a)  $\text{PbCl}_2$  powder, b)  $\text{PbO}$  powder.
- Figure 3. Raman spectrum of  $\text{PbCl}_2$  powder containing 0.95%  $\text{PbO}$  powder.
- Figure 4. Raman spectra of Pb sample surfaces immersed in solution, a) sample exposed to aerated 0.1M  $\text{HCl}$  solution for 7 days, b) sample exposed to deoxygenated 0.1M  $\text{HCl}$  solution for 12 days.
- Figure 5. Raman spectra of a) Pb sample immersed in aerated 0.1M  $\text{HCl}$  solution after 3 day exposure, b) Pb surface exposed to aerated 0.1M  $\text{HCl}$  solution for 3 days then dried in air.
- Figure 6. Raman spectrum of Pb surface immersed in 0.01M  $\text{NaOH}$  solution containing dissolved oxygen for 26 days.
- Figure 7. Raman spectrum of  $\alpha\text{-Fe}_2\text{O}_3$  powder.





SIDE VIEW



TOP VIEW

